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## REE-FERRITE BASED CERAMIC

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Fine REE-ferrite powders were obtained by wet burning. The solid-phase synthesis of lanthanum – gadolinium ferrite was studied. It was shown that the desired phase can be obtained at temperatures to 750°C. Firing regimes making it possible to obtain REE-ferrite based ceramic with low open porosity and relative density to 99% of the theoretical value were found.

**Key words:** matrix material, actinides, perovskite, ferrites, aluminates, REE.

One of the main problems of atomic energy is handling liquid high-level wastes (HLW), which are by-products of radiochemical reprocessing of spent nuclear fuel from nuclear power plants. The long-lived radionuclides ( $T_{1/2} > 15$  yr) present in HLW can be divided into two groups: fission products and transuranium elements. Previous work [1] has shown that the second group is much more dangerous than the first one, and to optimize the storage time and mass of the stored wastes it is desirable to separate out the actinide fraction of the HLW, which depending on the technological process will consist partially or entirely of lanthanides — fission products. It has been shown [2] that perovskite with the composition  $M^I M^{II} O_3$ , where  $M^I$  is a metal ion with ionic radius of about 1 Å and  $M^{II}$  is a metal ion with radius close to the ionic radius of titanium in naturally occurring perovskite ( $CaTiO_3$ ) — 0.64 Å, can be used to immobilize the actinide fraction. The total charge of the ions must be 6 in order to compensate the oxygen charge. Because large amounts of actinides are present in the HLW they can comprise the base of the matrix, while trivalent Fe ions (0.67 Å) can be used for  $M^{II}$ .

One technique commonly used to synthesize the matrix is briquetting by uniaxial pressing followed by sintering. This technique is distinguished by simplicity of the equipment and low cost compared with other methods (for example, hot pressing or induction melting). The object of the present work was to obtain and investigate the properties of ceramic based on lanthanum and gadolinium oxides with the compositions  $LaFeO_3$  and  $La_{0.6}Gd_{0.4}FeO_3$ . The latter composition is chosen because the average ionic radius of the cations in the  $M^I$  position (1.00 Å) is close to the average ionic

radius of the elements in the actinide fraction of HLW (0.999 Å), containing lanthanides (from La to Tb) and trivalent actinides (predominately Am and Cm).

The wet burn method was chosen to obtain the initial powders for synthesizing the ceramic [3, 4]. This method consists of heating a mixture of solutions of metal nitrates with a reducing agent, which can be, for example, citric acid, aminoacetic acid (glycine),  $\beta$ -alanine, hydrazine nitrate, and so forth.

Chemically pure lanthanum and iron (III) nitrates were used as the initial compounds. Gadolinium nitrate was obtained by dissolving its oxide in nitric acid. A weighed amount of glycine (molar ratio  $Gly : NO_3^- = 1.2$ ) was added to a mixed solution of metal nitrates. The solution was evaporated to dryness in a quartz vessel, placed inside a tubular furnace at temperature 280 – 300°C. An exothermal redox reaction, accompanied by heating of the reaction mixture and the release of a large quantity of gaseous products, completed the process. The synthesized powder was kept in a muffle furnace for 1 h at 750°C to remove the products of glycine decomposition and carbon burn-out.

The average size of the powder particles, calculated from the specific surface area of the powder (19 – 20 m<sup>2</sup>/g), was 47 nm. This value agrees well with the scanning electron microscopy (SEM) data (Fig. 1).

X-ray phase analysis of the initial powders, calcinated for 1 h at different temperatures, showed that the phases of the ferrites  $LaFeO_3$  and  $La_{0.6}Gd_{0.4}FeO_3$  with an orthorhombic unit cell form even during pyrolysis (to 750°C). As temperature is increased to 1200°C the phase composition of the powder remains unchanged (Fig. 2). The reflections of the individual oxides  $La_2O_3$ ,  $Fe_2O_3$ , and  $Gd_2O_3$  were not seen in any diffraction pattern.

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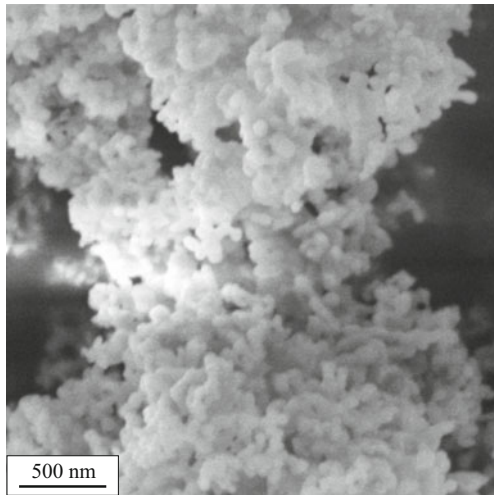


Fig. 1. SEM image of  $\text{LaFeO}_3$  powder.

The powders obtained were disaggregated in a planetary mill by the wet method for 1 h (balls : material : water = 30 : 1 : 1). Laser-diffraction measurements showed that the average particle size was  $0.76 \mu\text{m}$  and that the 90% of the particles did not exceed  $1.8 \mu\text{m}$  in size.

A solution of polyvinyl alcohol with content 3 wt.% (2 – 2.5% in terms of the dry press powder) was introduced into the suspension, which was dried at  $100^\circ\text{C}$  to residual moisture content 10 – 12%. The prepared powders were molded by uniaxial pressing under pressure 360 MPa into 1 – 2 mm thick and 12 mm in diameter cylindrical pellets or  $4 \times 4 \times 60$  mm rectangular bars.

It is well known that the previous heat-treatment history of the initial powder strongly affects the behavior of the pressed samples during calcination. A series of experiments with  $\text{La}_{0.6}\text{Gd}_{0.4}\text{FeO}_3$  stoichiometric powder was conducted to find the optimal temperature for the preliminary calcination. The powder obtained by wet burning was kept standing for 1 h at  $750^\circ\text{C}$  and then additionally for 1 h at different temperatures (from 900 to  $1100^\circ\text{C}$ ). The heat-treated powders were disaggregated in a planetary mill, a temporary technological binder was added, and blanks were pressed, as described above.

The behavior of the samples during calcination was studied by dilatometry, i.e., by recording the shrinkage curves as the samples were uniformly heated at a prescribed tempera-

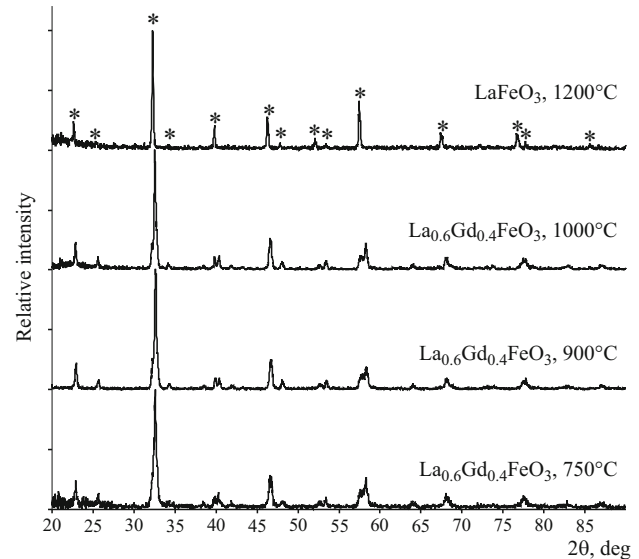


Fig. 2. X-ray diffraction patterns of  $\text{LaFeO}_3$  and  $\text{La}_{0.6}\text{Gd}_{0.4}\text{FeO}_3$  powders calcinated at different temperatures: \*)  $\text{LaFeO}_3$  phase with orthorhombic symmetry.

ture. The temperature  $t_{\max \text{ dI/dt}}$  at the maximum rate of shrinkage and the temperature  $t_{\text{shr. onset}}$  of shrinkage onset are presented in Table 1.

The ferrite ceramic samples start to shrink in the temperature range  $1000 - 1045^\circ\text{C}$ . The shrinkage onset temperature is minimal ( $1000^\circ\text{C}$ ) for blanks pressed from powder heat-treated at  $1000^\circ\text{C}$ . This is  $25^\circ\text{C}$  lower than for powder heat-treated at  $900^\circ\text{C}$  and  $45^\circ\text{C}$  lower than for powders heat-treated at 750 and  $1100^\circ\text{C}$ . The temperature corresponding to the highest shrinkage rate is minimal ( $1160^\circ\text{C}$ ) for the sample fabricated from powder heat-treated at  $900^\circ\text{C}$ . Thus, the compaction rate of this sample is maximal at a lower temperature. For this reason the heat-treatment temperature  $900^\circ\text{C}$  was chosen as optimal and used in subsequent experiments on optimizing the kilning regime.

The sinterability of lanthanum ferrite  $\text{LaFeO}_3$  and lanthanum-gadolinium ferrite  $\text{La}_{0.6}\text{Gd}_{0.4}\text{FeO}_3$  ceramics was studied. The variable parameter in these experiments was the isothermal soaking temperature. The soaking time (3 h) and the temperature rise rate (5 K/min) were constants. The results for the kilning regimes are presented in Fig. 2. The radial shrinkage  $\Delta D$ , the water absorption  $W$ , the open porosity  $P_{\text{op}}$ , and the density  $\rho$  were used as the parameters for making comparisons. The theoretical density was calculated using the unit cell parameters calculated from the diffraction data. The values for  $\text{LaFeO}_3$  and  $\text{La}_{0.6}\text{Gd}_{0.4}\text{FeO}_3$  are  $6.646$  and  $7.004 \text{ g/cm}^3$ , respectively.

The ceramic with the composition  $\text{La}_{0.6}\text{Gd}_{0.4}\text{FeO}_3$  reaches relative density 99% of the theoretical value and open porosity of no more than 0.7% at temperature  $1250^\circ\text{C}$ . The grain size obtained under these conditions is  $1 - 3 \mu\text{m}$  (Fig. 3). Further increasing the kilning temperature does not greatly change the properties of such a ceramic.

TABLE 1. Temperature at Maximum Shrinkage Rate  $t_{\max \text{ dI/dt}}$  and Shrinkage Onset  $t_{\text{shr. onset}}$

Heat treatment, $^\circ\text{C}$	$t_{\max \text{ dI/dt}}, ^\circ\text{C}$	$t_{\text{shr. onset}}, ^\circ\text{C}$
750	1180	1045
900	1160	1025
1000	1190	1000
1100	1200	1045

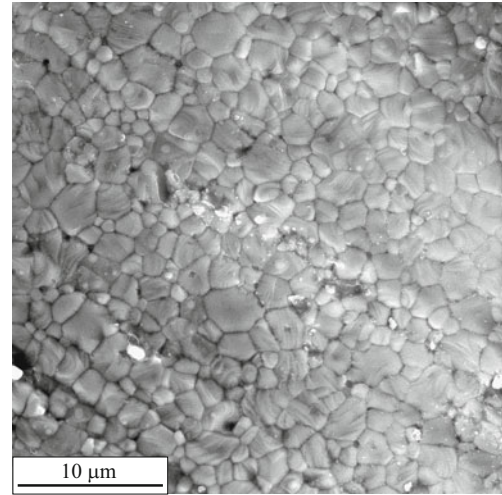
**TABLE 2.** Ceramic Properties for Different Kilning Temperatures

Ceramic	Kilning temperature, °C	$\Delta D$ , %	$W$ , %	$P_{op}$ , %	$\rho$ , g/cm <sup>3</sup> (%) <sup>*</sup>
$\text{La}_{0.6}\text{Gd}_{0.4}\text{FeO}_3$	1175	13.5	2.21	13.3	6.020 (86%)
	1200	16.1	0.31	2.0	6.634 (95%)
	1250	15.2	0.10	0.7	6.942 (99%)
	1300	15.2	0.10	0.7	6.603 (94%)
	1350	16.1	0.10	0.7	6.708 (96%)
	1400	15.0	0.22	1.5	6.761 (97%)
$\text{LaFeO}_3$	1175	15.0	0.12	0.8	6.211 (94%)
	1200	15.3	0.08	0.5	6.630 (99.5%)
	1250	14.5	0.00	0.0	6.409 (97%)
	1300	13.7	0.04	0.3	6.569 (99%)
	1350	14.3	0.06	0.4	6.244 (94%)

\* Percentage of the theoretical density.

Ceramic made from pure lanthanum ferrite (no gadolinium) reaches relative density 99.5% for the theoretical value and open porosity no more than 0.5% at the lower temperature 1200°C. In addition the ceramic with low open porosity (< 1%) can be obtained at even lower temperature 1175°C. Increasing the kilning temperature to 1350°C does not greatly change the relative density and open porosity of the ceramic.

In summary, a ceramic based on REE ferrites with the optimal kilning regime 1200 – 1250°C, 3 h was obtained. The porosity of the ceramic obtained under these conditions is low — to 0.7% and the relative density reaches 99% of the theoretical value.

**Fig. 3.** SEM image of a  $\text{La}_{0.6}\text{Gd}_{0.4}\text{FeO}_3$  surface (1250°C).

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